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(54) Title: MICROBICIDAL COMPOSITIONS AND METHODS

(57) Abstract

Microbicidal compositions comprising aliphatic peracids, the corresponding aliphatic acid, hydrogen peroxide and optionally one or more other aliphatic acids having a mole ratio of aliphatic acid to peracid of greater than 5:1 are provided. The compositions have improved activity as virucides, superior stability when diluted with hard water, improved residual activity and superior disinfection and vegetable quality in vegetable disinfection. Preferably, the peracid is peracetic acid and the optional aliphatic acid is acetic acid or propionic acid.

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Microbicidal Compositions and Methods

The present invention concerns microbicidal compositions and methods. More specifically, the present invention concerns microbicidal compositions and methods employing aliphatic peracids as microbicide.

The use of aliphatic peracids as microbicides is well known in the art. Such solutions have found favour because they offer a microbicidal system which has reduced environmental impact and are completely biodegradable.

Many of the micro-organisms on which aliphatic peracids have an fall into the classes of bacteria and viruses. In particular, the reduction in numbers of viruses is important in controlling or reducing the spread of disease, especially in areas where there is a risk of cross-infection, for example in hospitals and clinics. In such areas, it is advantageous if the activity of a microbicidal composition can be improved as it either allows greater reductions in numbers of micro-organisms for a given treatment, thus reducing the risks of infection, or allows more cost-effective use of the treatment.

In many applications of aliphatic peracids, the peracid is supplied as a relatively concentrated solution, and is diluted just prior to use to a concentration that will give good activity in the chosen application. In many cases, it is convenient to dilute with mains water supplied to the site of use, which, in many parts of the world, can contain significant levels of cations, particularly calcium and magnesium ions, which make the water "hard". The presence of hardness ions has been shown in the course of the studies leading to the present invention to reduce the stability and hence the efficacy of aliphatic peracids, and although the effect of the hardness ions can to a certain degree be ameliorated by the inclusion in the formulation of a sequestrant for water hardness, eg EDTA, the benefit is somewhat limited. In any event, the use of sequestrants at levels that would significantly ameliorate the problems

caused by hard water adds to the cost of the formulations, and is less favoured as it can also result in the sequestrant solubilising normally insoluble toxic heavy metals present in the natural environment, encouraging their entry into the water system.. It would therefore be advantageous to identify aliphatic peracid compositions intrinsically having improved stability in hard water, in the absence of or in addition to that obtained by the incorporation of a sequestrant.

The microbicidal activity of aliphatic peracids is believed to derive from the oxidation of chemical components of micro-organisms, and so the peracid is decomposed during such action. As such, the activity of solutions containing peracids as the only active component is normally restricted by the stability of the peracid in use. The mechanism of action of peracids means that they are very suitable for use in shock treatment regimes wherein the levels of micro-organism are reduced significantly by periodic dosing. In cases where the substrate that has been treated with a shock dose of peracid is subject to re-contamination during eg storage or further processing, the numbers of micro-organisms can rapidly reach similar levels to those prior to the treatment, thus necessitating further treatment. It would therefore be desirable to reduce the frequency of these chemical treatments by providing an aliphatic peracid system which maintains its anti-microbial activity over an extended period.

It is an object of certain aspects of the present invention to provide aliphatic peracid solutions having improved activity against viruses.

It is a further objective of some aspects of the present invention to provide aliphatic peracid solutions having improved stability when diluted with hard water.

It is another objective of particular aspects of the present invention to provide aliphatic peracid solutions having residual anti-microbial activity.

According to one aspect of the present invention, there are provided compositions comprising an aqueous solution of an aliphatic peracid, the corresponding aliphatic acid, hydrogen peroxide, and optionally one or more other aliphatic acids, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a second aspect of the present invention, there are provided compositions with improved activity against viruses which comprise an aqueous solution of at least one aliphatic peracid, at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a third aspect of the present invention, there are provided compositions with improved stability when diluted with hard water which comprise an aqueous solution of at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a fourth aspect of the present invention, there are provided compositions with improved residual activity which comprise an aqueous solution of at least one aliphatic peracid, at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a fifth aspect of the present invention, there is provided a virucidal process in which a virus is contacted with an aqueous solution which comprises at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a sixth aspect of the present invention, there is provided a process for producing a dilute aqueous solution of an aliphatic peracid having improved stability in which a concentrate containing an aliphatic peracid, aliphatic acid and hydrogen peroxide is diluted with hard water, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

According to a seventh aspect of the present invention, there is provided a microbicidal process having improved residual activity in which a substrate which may be contaminated by micro-organisms is contacted with an aqueous solution which comprises at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acids to peracid is greater than 5 : 1.

According to an eighth aspect of the present invention there is provided a process for the disinfection of fruit and vegetables, employing as a disinfectant an aqueous solution which comprises at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acids to peracid is greater than 5 : 1.

The aliphatic peracid can be any aliphatic peracid that has a disinfectant effect. However, in many embodiments, the aliphatic peracid is selected from the group containing soluble peracids, which may include low molecular weight aliphatic peroxyacids, for example containing up to 6 carbon atoms, of which especially preferred examples comprise peracetic acid and perpropionic acid. Other examples include perbutyric acid, persuccinic acid, perglutaric acid and

peradipic acid, particularly mixtures of persuccinic, perglutaric and peradipic acids. The peracid may alternatively be selected from hydroxy-peracids, for example percitric or pertartaric acid. In most preferred embodiments, the peracid is peracetic acid.

The other aliphatic acids which are optionally included in the compositions according to the present invention are selected from the group containing from 1 to 6 carbon atoms, and are preferably acetic or propionic acid.

The compositions according to the present invention and employed in processes according to the present invention are often solutions comprising an equilibrium mixture of an aliphatic peracid, the corresponding aliphatic acid, hydrogen peroxide, water and, when optional additional aliphatic acids are also present, the corresponding peracid.

In many embodiments, aliphatic peracids comprise greater than about 0.1% by weight of the composition, often from about 0.5% to about 20% by weight, and most often from about 1 to about 15% by weight.

In compositions according to the present invention, the mole ratio of aliphatic acid to peracid is greater than 5 : 1. In many embodiments, the mole ratio is from about 10 : 1 to about 40 : 1, and some preferred embodiments, the mole ratio is from about 13 : 1 to about 25 : 1.

Hydrogen peroxide typically comprises from about 0.5 to 20% by weight of the compositions according to the present invention, often from about 0.75 to about 15%, and most often from about 1 to about 10% by weight. It will be recognised by one skilled in the art that for an equilibrium peracid solution having a high ratio of aliphatic acid to peracid, the concentration of hydrogen peroxide necessary to give an equilibrium composition is often very much lower than for an equilibrium composition having a lower ratio of aliphatic acid to peracid. This means that for compositions having equivalent available oxygen, a greater proportion of the active oxygen is present in the more microbicidally active component ie the peracid if there is a lower concentration of hydrogen peroxide than if there is a higher concentration of hydrogen peroxide. Thus, compositions according to the present invention will usually have a greater microbicidal activity for a given active oxygen concentration than compositions not according to the present invention.

The compositions according to the present invention often additionally comprise one or more stabilisers to further prolong the storage stability of the peracid. Such stabilisers are well known in the art, and often comprise alkyleneaminopolymethylene phosphonic acids, eg cyclohexyldiaminomethylene

phosphonic acid and its salts or hydroxyethylidene diphosphonic acid or salts thereof.

Other optional components of compositions according to the present invention are mineral acids, especially sulphuric, phosphoric and nitric acid, which are often employed as catalysts to speed the equilibration of the compositions during manufacture, corrosion inhibitors, wetting agents, thickeners, dyes and perfumes.

Suitable corrosion inhibitors can be selected from the group consisting of alkali metal phosphate salts, especially disodium and dipotassium hydrogenphosphate, triazoles, phosphonates, especially cyclohexyldiaminomethylene phosphonic acid and its salts.

These optional components can also be employed separately from the compositions according to the invention by supplying a two pack system in which one solution is a composition according to the present invention and the other is a solution of other components. These two packs can then both be diluted in the same solution to form a further composition, also according to the present invention. Such an approach has the advantage that it is possible to include in the diluted composition components with desirable properties that would adversely affect the storage stability of the peracid solution over an extended period, but which do not significantly affect the stability of the peracid over the storage period of the diluted solution, which is often less than that of the non-diluted compositions, or at the concentration in the dilution.

Wetting agents can be either anionic, cationic, amphoteric or nonionic. Particularly suitable wetting agents are alkaryl sulphonic acids or their salts, and alcohol ethoxylates.

The compositions according to the present invention can conveniently be prepared by mixing an organic acid or anhydride with hydrogen peroxide in aqueous solution, in the presence of any additional components, at a temperature in the region of from 10°C to about 50°C and allowing to reach equilibrium.

The compositions according to the present invention can be employed as anti-viral agents, especially in the field of medical instrument disinfection. When employed in such an application, the compositions are often diluted just prior to use. The dilution is chosen to be such that the concentration of peracid can often be up to about 2% by weight, although the concentration is usually from about 0.001% to about 1%, preferably from about 0.002% to about 0.75%. Often, the dilution is by a factor of from about 10 times to

about 10,000 times, more often from about 25 times to about 5,000 times, depending on amongst other factors, the concentration of peracid in the starting composition.

The temperature employed for use of the composition is often greater than about 10°C, often between about 15°C and 75°C, more often between about 17°C and 35°C. It is particularly preferable that the compositions are employed at ambient temperature, and so it will be recognised that this can vary significantly, although the temperature is often likely to be controlled to a certain extent by the use of, for example, air conditioning.

The compositions can be employed as virucidal agents on or in a wide range of articles, surfaces or media that are contaminated with viruses, and may also be employed on objects where there is a risk of virus contamination. They are particularly suited to the disinfection of hard surfaces and objects containing metal, especially aluminium, brass, copper and steel. The compositions are also suited to the disinfection of cloth articles, for example medical dressings, and aqueous media.

The compositions can be applied to the article or surface in a large number of ways. For example, they can be sprayed or can be wiped using a suitable distributor, eg a cloth. In many embodiments, however, the compositions are employed as a soak bath in which the article to be disinfected is immersed in the bath, and then rinsed after treatment to remove substantially all of the disinfectant.

The contact period employed can vary widely depending on the area of application, and the concentration of disinfectant. In many embodiments, the contact period is greater than about 30 seconds. In certain preferred embodiments, the contact period is from about 1 minute to about 60 minutes, although it will be recognised that periods significantly longer than this may be employed in cases where the compositions are employed as a soak bath, for example, up to 24 hours or more.

In many applications where the peracid solution is in the form of a relatively concentrated solution which is diluted with water prior to use, it is desirable that the dilute solution produced is employed within a reasonably short period after dilution because, unless the dilution water has been treated to remove impurities prior to use as a diluent, the impurities present in the water can cause a significant reduction in the peracid concentration, and thus reduce the effectiveness of the solution. Typical of the impurities which can cause such a

decomposition are those which are the cause of water hardness, for example, divalent metal carbonate or bicarbonate salts.

It has been surprisingly found that when compositions according to the present invention are diluted with hard water, ie water containing greater than about 75ppm and up to about 1500ppm (expressed as $CaCO_3$) of hardness, the solutions produced have improved stability when compared to similar dilutions of peracid compositions not according to the present invention.

It will be recognised that less attention has been paid to improving the stability of solutions that are diluted just prior to use compared with solutions prepared for long term storage, where the peracid should desirably be retained for several months. In many cases, it is preferable for the peracid in solutions diluted just prior to use to be stable for a period of several days depending on the application, sometimes up to 10 days, often up to 6 days and in many instances up to 3 days.

The peracid solutions prepared just prior to use can have a very wide range of peracid concentrations depending on the application, and the conditions under which they are to be applied. The concentration of peracid can often be up to about 2% by weight, although the concentration is usually from about 0.001% to about 1%, preferably from about 0.002% to about 0.75%.

In many applications for peracid solutions, particularly disinfectant applications, the solution is employed as a shock treatment and is required to have a rapid biocidal effect without any need for residual activity. However, in certain applications, particularly where the substrate is subject to re-contamination, for example when the substrate is recycled aqueous process liquors as in the paper industry or in cooling water treatment, it is advantageous if the solution has activity which remains beyond the normal activity period of the peracid alone. In many instances, the recycled process liquors are subject to regular shock treatment, but there are often periods when the shock treatment biocide is less effective and so unless all the micro-organisms have been killed, the microbial numbers can increase. Also in these less effective periods, the disinfectant can often be insufficiently active to control fresh microbial contamination. In these cases, it is often not necessary for the residual activity to be sufficient to have a significant biocidal effect; it is sufficient for the residual activity to be sufficient to prevent or inhibit significant increases in the microbial population, ie to be biostatic.

It has been surprisingly found that the peracid compositions according to the present invention have superior residual microbicidal activity, and also that

their performance as a shock treatment are improved when compared to similar peracid compositions not according to the present invention.

It will be recognised that the concentration of peracid employed in applications as a shock treatment with residual activity can vary widely depending on application and the conditions under which it is employed. The concentration of peracid is often up to about 2% by weight, although the concentration is usually from about 0.001% to about 1%, preferably from about 0.002% to about 0.75%.

There are many areas of application for compositions according to the present invention where the improved residual activity is of advantage. Examples include the disinfection of sugar beet process liquors, cooling water and other circulating water systems, aqueous pulp and paper process liquors, animal feed and grain.

The peracid compositions may be dosed manually, but in many embodiments, the dosing is automatically controlled by the use of a metering pump and a suitable control system which can deliver the peracid according to a pre-determined programme. The peracid can be dosed in a number of different ways, for example as a liquid or as a spray by using suitable equipment known in the art.

Another area of application for compositions according to the present invention is in the area of fruit and vegetable disinfection. Peracid systems are well known for disinfection in this area, either alone or in a two stage process in combination with a reducing agent which prevents excess peracid from oxidising and discolouring the fruit or vegetable being disinfected. The concentration of peracid is often up to about 0.2% by weight, although the concentration is usually from about 0.0001% to about 0.1%, preferably from about 0.0005% to about 0.05% by weight.

Typical reducing agents include alkali metal salts of sulphite, metabisulphite and thiosulphate, ascorbic acid and such like, with the most preferred reducing agent being sodium thiosulphate. The concentration of reducing agent employed is typically chosen to ensure adequate removal of excess peracid and so the concentration can vary quite widely depending on, for example, the concentration of peracid employed. In many cases, the concentration of reductant solution is in the range of from about 0.5g/l to about 50g/l, preferably from about 1g/l to about 10g/l.

It has surprisingly been found that peracid compositions according to the present invention give superior disinfection and residual activity compared to

peracid compositions not according to the present invention. Use of compositions according to the present invention in a two stage process with sodium thiosulphate as reducing agent also surprisingly gives superior fruit and vegetable appearance after storage for up to 5 days, particularly in the case of lettuce disinfection.

The treatment time for use of compositions according to the present invention in fruit and vegetable disinfection is often from about 1 minute to about 60 minutes, and is most often from about 2 minutes to about 30 minutes. When a reductant is employed, the contact time for the reductant is often from about 1 minute to about 30 minutes, most often from about 2 minutes to about 15 minutes. The temperature at which the disinfection and any subsequent reduction stage take place can vary over a wide range, but is often ambient temperature, and so is usually likely to range from about 10°C to about 30°C in the United Kingdom, but may differ in other countries.

Having described the invention in general terms, embodiments of the invention will now be described more fully by way of example only.

Example 1. Preparation of Peracid Composition according to the present invention.

50.85g of glacial acetic acid, 38.05g of demineralised water, 11.1g of 35% w/w hydrogen peroxide solution, 1.0g 50% w/w hydroxyethylidenedimethylene phosphonic acid solution, 0.15g of dipicolinic acid solution (10% w/w in 5% w/w NaOH solution) and 0.7g of 98% w/w sulphuric acid solution were mixed at room temperature. After 1 week, the solution was analysed as having the following composition (all % by weight):

Peracetic Acid	3.89%
Hydrogen Peroxide	2.21%
Acetic Acid	52.52%
Mole Ratio of Peracid : Acid	17 : 1

Example 2. Activity against Viruses

A stock of Polio 2 virus containing 1.8×10^8 plaque forming units per ml (pfu/ml) was treated in a disinfection suspension test at room temperature (about 20 - 25°C) in the presence of horse serum (10%v/v) with a solution of peracetic acid according to the present invention of formula A below, and also with a solution of peracetic acid not according to the invention of formula B below. The two solutions were each diluted to give applied peracetic acid concentrations of 800ppm and 1600ppm. Contact times of both 5 and 10 minutes were evaluated. Neutralisation after the contact time was by 1/10th dilution in 5% w/v sodium thiosulphate solution also containing 0.025%w/v catalase. Surviving polio virus was then evaluated by plaque assay according to the method given by Morris and Waite, "Evaluation Procedures for the Recovery of Viruses from Water. II Detection Systems", Water Research, 1980, Vol 14, pp795-8 on the Buffalo Green Monkey cell line and the Logarithmic Reduction Factor (LRF) calculated. The results are given in Table 2 below.

Table 1 Peracetic Acid Formulations (All % w/w)

Formulation	% PAA	%AA	$\%H_2O_2$	Mole Ratio AA : PAA
A	4	47	2	15 : 1
B	5	8	20	1.6 : 1

AA = acetic acid; PAA = peracetic acid

Table 2 Activity of Peracetic Acid Solutions against Polio virus

Formulation	Concentration	LRF after time (minutes)	
		5	10
A	800	4.1	5.4
A	1600	Total Kill	Total Kill
B	800	1.9	2.4
B	1600	3.2	4.0

The results given in Table 2 clearly show that at both concentrations of peracetic acid, the virucidal performance of Formulation A (according to the present invention) is greatly superior to that of Formulation B (not according to the invention).

Example 3 Stability of Peracetic acid in Hard Water Dilutions

Samples of hard water containing 192 ppm permanent hardness, and 202 ppm temporary hardness (expressed as $CaCO_3$) were inoculated to a concentration of peracetic acid of 20 ppm by dilution by 2,500 and 2,000 times respectively of peracetic acid samples of formulations A and B in Example 2 above. The concentration of peracetic acid in each of the samples was measures at intervals over 24 hours by iodometric titration in ethane-1,2-diol at $<-10^{o}C$ with sodium thiosulphate solution. The results are given in Table 3 below.

Table 3 Stability of Peracetic Acid in Hard Water

	Peracetic Acid Concentration (ppm)	
Formulation	A	B
0	20	20
1 min	16.2	5.3
30 min	14.8	4.2
120 min	14.5	1.8
24 hrs	7.1	-

The results in Table 3 clearly show that for 20 ppm peracetic acid, the stability of formulation A (according to the present invention) is superior to the stability of formulation B (not according to the present invention) when the formulations are diluted with hard water.

Example 4 Residual Activity of Peracetic Acid

The residual activity and disinfection performance of the formulations given in Table 4 below were evaluated in a suspension test against a mixed culture of 4 asporogenous bacteria, Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Streptococcus faecalis, as an initial inoculum of 1.3 x 10^6 colony forming units/ml (cfu/ml), and as a rechallenge inoculum of 2.6 x 10^3 cfu/ml after 2 days, and 2.1 x 10^3 cfu/ml after 9 days. The conditions employed were a temperature of 20°C, water having 100 - 120 ppm hardness as $CaCO_3$, and in the presence of 4 g/l yeast extract.

The viable cell counts were determined after contact times of 10 minutes, and then at intervals over 14 days by one tenth dilution into a universal neutraliser containing 0.25% w/w catalase to prevent further activity and then by decimal dilutions of the neutraliser with Maximal Recovery Diluent. The dilutions were plated out on Plate Count Agar, incubated for 48 hrs at 37°C, and the plate counts measured. The results are given in Table 4 below.

Table 4. Results of Disinfection and Residual Activity Trial

In the table, AA = acetic acid; PA = propionic acid; PAA = peracetic acid

Formulation	Acid:PAA Mole ratio	Number of Viable Organisms after (time) cfu/ml					
		10 min	1 day	3 days	9 days	10 days	14 days
Water only	-	3.3×10^{6}	6.7×10^{8}	3.5×10^{9}	4.7×10^{9}	6.5×10^{9}	7.3×10^{9}
500ppm AA	-	3×10^{6}	2.4×10^{6}	3.7×10^{7}	3.1×10^{8}	2.9×10^{8}	4.1×10^{7}
500ppm PA	-	3.8×10^{6}	3.4×10^{6}	5×10^{7}	2.4×10^{8}	2.2×10^{8}	4.8×10^{7}
30ppm PAA +56ppm AA	2.4:1	2.4×10^{3}	1.9×10^{4}	2.3×10^{9}	5.1×10^{9}	5.1×10^{9}	6.9×10^{9}
30ppm PAA +500ppm PA +56ppm AA	19.5:1	460	<10	860	9.2×10^{5}	7.2×10^{6}	9×10^{5}
30ppm PAA +556ppm AA	23.5:1	160	<10	685	7.6×10^{3}	2.5×10^{4}	3.9×10^{6}

The results given in Table 4 show that the compositions according to the present invention, ie those with a mole ratio of aliphatic acid to peracid of greater than 5 : 1 give superior initial disinfection compared to the composition not according to the present invention. This is surprising as the acids alone do not have any significant disinfectancy. The good residual activity of compositions according to the present invention is clearly demonstrated by the results for 3 days. These results are 24 hours after a challenge with 2.6×10^{3} cfu/ml. The results for both compositions according to the present invention are extremely low compared to the results for the other compositions. A similar pattern of results is demonstrated for the results after 10 and 14 days, showing the consistently better performance of compositions according to the present invention.

Example 5. Vegetable Disinfection.

Samples of chopped iceberg lettuce were contacted for 5 minutes at room temperature with peracetic acid solutions prepared by diluting compositions of formula A and B above, and formulation C below with water having 134ppm permanent and 180ppm temporary hardness as $CaCO_3$ to give the concentrations of peracid given in Table 5 below. After the contact time, the lettuce was washed for 2 minutes with a 5g/l sodium thiosulphate solution rinse. The samples were stored for 3 days at 4°C, and then their physical appearance and bacterial count determined. The bacterial count was obtained by stomaching 10g of lettuce in MRD, then serial dilution in MRD, and then plating out on Plate Count Agar for 2 days incubation at 30°C. The results are given in Table 5 below, expressed as a Log Reduction Factor (LRF) over an untreated control.

Table 5. Results of Vegetable Disinfection Trial

The control had 8.4×10^5 colony forming units per cm^3 after 3 days

Formulation	PAA Concentration	LRF after 3 Days
A	50 ppm	1.81
B	50 ppm	0.16
C	50 ppm	1.09
A	100 ppm	2.92
B	100 ppm	0.97
C	100 ppm	1.78

Formulation	% PAA	%AA	%H2O2	Mole Ratio AA : PAA
C	1	9	6	11.4 : 1

The results of this trial show that the results obtained in vegetable disinfection are significantly better in terms of microbial contamination and physical condition for formulations A and C (according to the present invention), particularly for formulation A, than the results for treatment with formulation B (not according to the present invention).

Example 6. Bacteriostatic Performance

100 ppm peracetic acid solutions were produced by aqueous dilution of peracetic acid formulations according to formulations A (according to the invention) and B (not according to the invention) in Example 2 above. In addition, a 100 ppm peracetic acid solution was produced by aqueous dilution of a third formulation, D. Formulation D (not according to the invention) comprised 15% w/w peracetic acid, 14% w/w hydrogen peroxide and 28% w/w acetic acid, with a mole ratio of acetic acid to peracetic acid of 2.4 : 1. The solutions were evaluated in duplicate for bacteriostasis against Pseudomonas aeruginosa and Staphylococcus aureus in the German DGHM Standard Method. The results are given in Table 6 below, where a "-" indicates no growth and a "+" indicates growth.

	Pseudomonas aeruginosa		Staphylococcus aureus	
Duplicate	1	2	1	2
Formulation				
A	-	-	-	-
B	+	+	+	+
D	+	+	+	+

From the results in Table 6, it can clearly be seen that the composition according to the present invention, formulation A was the only formulation that gave bacteriostasis.

Claims

1. Compositions comprising an aqueous solution of an aliphatic peracid, the corresponding aliphatic acid, hydrogen peroxide, and optionally one or more other aliphatic acids, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

2. Compositions with improved activity against viruses which comprise an aqueous solution of at least one aliphatic peracid, at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

3. Compositions with improved stability when diluted with hard water which comprise an aqueous solution of at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

4. Compositions with improved residual activity which comprise an aqueous solution of at least one aliphatic peracid, at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

5. A virucidal process in which a substrate which may be contaminated with viruses is contacted with an aqueous solution of at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

6. A process for producing a dilute aqueous solution of an aliphatic peracid having improved stability in which a concentrate containing an aliphatic peracid, aliphatic acid and hydrogen peroxide is diluted with hard water, characterised in that the mole ratio of aliphatic acid to peracid is greater than 5 : 1.

7. A microbicidal process having improved residual activity in which a substrate which may be contaminated by micro-organisms is contacted with an aqueous solution of at least one aliphatic peracid at least one aliphatic acid and

hydrogen peroxide, characterised in that the mole ratio of aliphatic acids to peracid is greater than 5 : 1.

8. A composition or process according to any preceding claim characterised in that the peracid solution comprises up to about 2% by weight of the diluted solution.

9. A composition or process according to claim 8 characterised in that the peracid solution comprises from about 0.001% to about 1% by weight of the diluted solution.

10. A composition or process according to claim 9 characterised in that the peracid solution comprises from about 0.002% to about 0.75% by weight of the diluted solution.

11. A process for the disinfection of fruit and vegetables, employing as a disinfectant an aqueous solution of at least one aliphatic peracid at least one aliphatic acid and hydrogen peroxide, characterised in that the mole ratio of aliphatic acids to peracid is greater than 5 : 1.

12. A process according to claim 11 characterised in that the peracid solution comprises up to about 0.2% by weight of the diluted solution.

13. A composition or process according to claim 12 characterised in that the peracid solution comprises from about 0.0001% to about 0.1% by weight of the diluted solution.

14. A composition or process according to claim 13 characterised in that the peracid solution comprises from about 0.0005% to about 0.05% by weight of the diluted solution.

15. A composition or process according to any preceding claim, characterised in that the mole ratio of aliphatic acids to peracid is from about 10 : 1 to about 40 : 1.

16. A composition or process according to claim 15, characterised in that the mole ratio of aliphatic acids to peracid is from about 13 : 1 to about 25 : 1.

17. A composition or process according to any preceding claim in which the peracid is supplied as a dilutable concentrate, characterised in that the peracid comprises greater than about 0.1% by weight of the concentrate.

18. A composition or process according to claim 17 in which the peracid is supplied as a dilutable concentrate, characterised in that the peracid comprises from about 0.5% to about 20% by weight of the concentrate.

19. A composition or process according to claim 18 in which the peracid is supplied as a dilutable concentrate, characterised in that the peracid comprises from about 1% to about 15% by weight of the concentrate.

20. A process according to any one of claims 5 to 19, characterised in that the process is carried out at a temperature of greater than about 10°C.

21. A process according claim 6, characterised in that the hard water contains from about 75ppm to about 1500ppm water hardness, expressed as $CaCO_3$.

22. A process according to claim 11, characterised in that the peracid treatment is followed by a subsequent treatment with a reducing agent solution selected from the group consisting of alkali metal salts of sulphite, metabisulphite, thiosulphate; and ascorbic acid.

23. A process according to claim 22, characterised in that the reducing agent is sodium thiosulphate.

24. A process according to claim 22, characterised in that the reducing agent is employed at a concentration of from about 0.5g/l to about 50g/l.

25. A process according to claim 24, characterised in that the reducing agent is employed at a concentration of from about 1g/l to about 10g/l.

26. A process or composition according to any preceding claim, characterised in that the aliphatic peracid is selected from the group consisting of low molecular weight aliphatic peroxyacids containing up to 6 carbon atoms and hydroxy-peracids.

27. A process or composition according to claim 26, characterised in that the aliphatic peracid is selected from peracetic acid, perpropionic acid, perbutyric acid, persuccinic acid, perglutaric acid and peradipic acid.

28. A process or composition according to any preceding claim, characterised in that the or other aliphatic acid is acetic acid or propionic acid.

29. Any novel microbicidal process or composition substantially as described herein with reference to the Examples.

30. Any novel microbicidal process or composition substantially as described herein with reference to any novel feature or combination of features.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/01823

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A01N37/16 //(A01N37/16,59:00,37:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	S.S. BLOCK 'DISINFECTION, STERILISATION AND PRESERVATION' 1991 , LEA & FEBIGER , PHILADELPHIA pages 172-180 see page 176, column 2, line 10 - line 15 ---	1-30
X	EP,A,0 193 416 (L'AIR LIQUIDE) 3 September 1986 see examples ---	1-30
X	EP,A,0 370 850 (L'AIR LIQUIDE) 30 May 1990 see claims ---	1-30
X	WO,A,88 08667 (MINNTECH CORP.) 17 November 1988 see examples --- -/--	1-30

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 1993	0 8. 12. 93

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/01823

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 03590 (HENKEL) 21 March 1991 see example 1	1-30
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X,P	WO,A,92 19287 (SOLVAY INTEROX) 12 November 1992 see example 1	1-30

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/GB 93/01823

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